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TRIPLET EXTINCTION COEFFICIENTS OF SOME LASER DYES II

by

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TRIPLET EXTINCTION COEFFICIENTS OF SOME LASER DYES II

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We measured the triplet extinction coefficients ϵ_T over the laser action spectral region of DODC, DMC, Sulforhodamine B, Rhodamine 575, Coumarin 523, Coumarin 521, Coumarin 504, Coumarin 498, Coumarin 490, LD466, bis-MSB, BBO, and OLIGO415. We employed the different lines from an argon and a krypton ion cw laser for excitation. McClure's method was again employed to measure the triplet extinction coefficients. We provide a simplified derivation of McClure's equation. The triplet extinction coefficient of Rhodamine 575 was also measured by using the depletion method and improving it by reconstructing for true triplet-triplet absorption. The value obtained is in good agreement with the one obtained by McClure's method.

I. INTRODUCTION

We continued the measurement of triplet extinction coefficients ϵ_T of commercially available laser dyes. Because a considerable number of these dyes absorb light in the yellow and red spectral region of the spectrum, we employed both an argon ion cw laser and a krypton ion cw laser for excitation. We used the same experimental procedures for measuring the ϵ_T values as described in our previous report [1] and refer to this report as I in this paper. As was the case in I, only a fraction of the triplet extinction coefficients ϵ_T could be measured. This was attributable to either photodecomposition or too-low triplet optical densities OD_T . These low OD_T values are the result of very short triplet lifetimes. In I we expressed our concern that the ϵ_T values of the coumarin laser dyes obtained by the depletion method did not agree with the values obtained with McClure's method [2]. It is well known that when T-T absorption is overlapping S-S absorption, the depletion method will give inaccurate results [3].

The depletion method can be improved by reconstructing for true T-T absorption [3]. We employ a simplified version of a method suggested by Pavlopoulos [4]. For laser dyes, only weak T-T absorption is overlapping the fluorescence spectral region. This makes it possible to find the isospectic point λ_c , at which $\epsilon_S(\lambda_c) = \epsilon_T(\lambda_c)$. We applied the depletion method corrected for T-T absorption on Rhodamine 575.

II. SEMIRIGOROUS DERIVATION OF McCLURE'S EQUATION

With regard to McClure's equation [2]

$$\frac{1}{OD_T} = \left(\frac{1}{\epsilon_T N_S d} \right) \left(1 + \frac{A_i}{I_{ex}} \right) \quad (1)$$

we wish to emphasize the following two points.

A. As already noted, McClure's equation as presented in form (1) is very suitable to obtain ϵ_T values of organic compounds by varying the intensity of the excitation light I_{ex} (i.e., it is an intensity variation method for obtaining ϵ_T values). By plotting $1/OD_T$ versus $1/I_{ex}$, OD_T is emphasized at infinite I_{ex} . Therefore, employing cw lasers as excitation sources is very appropriate for the application of equation (1). By focusing cw laser light with the aid of a lens, very high I_{ex} values can be experimentally realized. This makes the $I_{ex} \rightarrow \infty$ extrapolation possible.

Besides applying equation (1) to obtain ϵ_T values of organic compounds, it is noteworthy that equation (1) answers the following important question for photophysics: How does an observed triplet (or other transient) optical density OD_T of a molecule depend on the intensity of the excitation light I_{ex} ? It provides derivation of the important relationship:

$$OD_T = f(I_{ex}) \quad (2)$$

where the molecule can exist in two different multiplicities.

B. The derivation of McClure's equation is based on kinetic considerations, such as the rate equations that cover activation and deactivation of an organic molecule in its singlet as well as its triplet manifold. Nevertheless, when one is applying equation (1) to obtain ϵ_T values, one is always concerned about the validity of the different kinetic assumptions used in [2] to derive equation (1). Is it possible to find a simpler way (using fewer assumptions) to obtain equation (1)?

We present the following semirigorous route. At small excitation intensities I_{ex} , OD_T should depend linearly on I_{ex} ; i.e.,

$$OD_T = A I_{ex} \quad (3)$$



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At a given concentration N_S of an organic compound and steadily increasing I_{ex} , OD_T will not forever increase, but will reach a limiting value OD_T^∞ . This will occur when all the molecules N_S have been converted to N_T . This will be the case for $I_{ex} \rightarrow \infty$.

$$OD_T = OD_T^\infty = N_T \epsilon_T d. \quad (4)$$

The simplest equation fulfilling conditions (3) and (4) is:

$$OD_T = \frac{AI_{ex}}{1 + BI_{ex}}; \quad (5)$$

with $OD_T^\infty = A/B$.

$$OD_T = \frac{OD_T^\infty BI_{ex}}{1 + BI_{ex}}. \quad (6)$$

Equation (6) is identical to equation (1). This is evident by forming $1/OD_T$.

III. IMPROVED DEPLETION METHOD

The depletion method for measuring triplet extinction coefficients has been applied extensively [3,5,6]. The advantage of this method is that it does not require any knowledge of the rate constants of the underlying radiationless transitions. The main weakness of the method is the requirement that no T-T absorption be present where the singlet depletion is measured. Unfortunately, this ideal situation is rarely encountered. One finds experimentally that there is at least some T-T absorption present (e.g. in laser dyes). In addition, the depletion method can often not be used when cw lasers are used as excitation sources [4,7]. The largest depletion effects are observed at the maxima of S-S absorption, which in the case of dyes is the lowest energy S-S absorption band. For obtaining large triplet optical densities OD_T , it is desirable to excite into the lowest-energy S-S absorption band. These two requirements result in unabsorbed cw laser radiation oversaturating the electronic detection system. Using a monochromator with a single grating (as was the case in our experiment), and exciting into the maximum of S-S absorption, one is often not able to perform measurements at the onset of S-S absorption

because excessive stray laser light is oversaturating the detection system. However, exciting at the short-wavelength side of the S-S absorption maximum, depletion at the onset of S-S absorption can be observed [4]. Employing a double monochromator, it should be possible to observe depletion at the onset of S-S absorption with cw laser excitation into the intensity maximum of S-S absorption.

By reconstructing for true T-T absorption, the shortcomings of the conventional singlet depletion method can be alleviated. We assume that the triplet extinction coefficient ϵ_T between points a and b varies linearly; i.e.,

$$\epsilon_T(\lambda) = A + \lambda B \quad (7)$$

or

$$OD_T(\lambda) = C + \lambda F . \quad (8)$$

However, if a linear relationship does not hold, one can use the next higher approximation:

$$\epsilon_T(\lambda) = G + \lambda H + J\lambda^2 \quad (9)$$

or

$$OD_T(\lambda) = J + \lambda M + N\lambda^2 . \quad (10)$$

Equations (8) and (10) hold for spectral regions where no S-S absorption is present. When S-S absorption is overlapping T-T absorption, we have [3],

$$OD_{S+T}(\lambda) = N_T d[\epsilon_T(\lambda) - \epsilon_S(\lambda)] . \quad (11)$$

Significantly, $OD_{S+T} = 0$ when

$$\epsilon_T(\lambda_c) = \epsilon_S(\lambda_c) . \quad (12)$$

This isospectric point λ_c can be rather accurately determined when cw lasers are employed as excitation sources [4]. Measuring $\epsilon_S(\lambda_c)$ at this wavelength therefore yields an accurate value of $\epsilon_T(\lambda_c)$. Extrapolating equations (8) or (10) from λ_b , the short distance to λ_c [assuming equations (7) or (9) hold] yields $OD_T(\lambda_c) = N_T \epsilon_T(\lambda_c) d$. N_T can be determined because $\epsilon_T(\lambda_c)$ is known.

IV. EXPERIMENTAL PROCEDURES

A. Spectroscopic equipment

We used the same spectroscopic setup as described in [7]. Both the Spectra Physics model 164 cw krypton and the model 2025-05 cw argon ion laser were used.

B. Chemicals

DODC, Sulforhodamine B, and DCM, were obtained from Eastman Kodak Company. bis-MSB was also obtained from Eastman Kodak Company and recrystallized from hexane. Rhodamine 575, Coumarin 523, Coumarin 521, Coumarin 504, Coumarin 498, Coumarin 490, and LD466 were purchased from Exciton. BBO was obtained from K&K Laboratories and was zone-refined several times. OLIGO415 was furnished by Kauffman.

With the exception of bis-MSB, OLIGO415, and BBO, the dyes were dissolved in ethyl alcohol (from U.S. Industrial Chemical Company) and methanol (from Aldrich Chemical Company) in the ratio 4:1. bis-MSB, OLIGO515, and BBO were dissolved in 2-methyltetrahydrofuran (from Lancaster Chemical Company).

V. RESULTS AND DISCUSSION

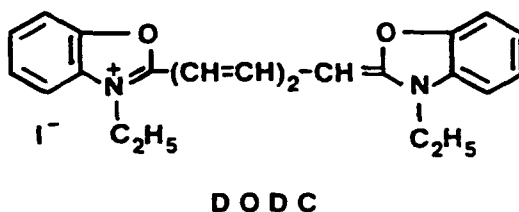
A. Triplet extinction coefficients

1. 3,3'-Diethyloxacarbocyanine iodide (DODC)

DODC has found applications in the dye laser field for mode locking Rhodamine 6G dye lasers [8-10]. Laser action under flashlamp excitation of this dye was reported by Maeda and Miyazoe [11]. ϵ_T values of this dye were obtained by Morrow et al. [12]. Conventional and dye laser flash photolysis was employed for excitation. To measure triplet extinction coefficient, the energy transfer technique method was employed [3]. As triplet donor, naphthalene was used. These experiments used dilute solutions (in the range of 10^{-6} molar) to avoid DODC dimer formation. A value of $\epsilon_T(670) = 95.5 \pm 9.5 \times 10^3$ l/mole cm was obtained. We have summarized our results.

Concentration N_S	$\epsilon_T \times 10^{-3}$
2.00×10^{-4} molar	10.6
1.04×10^{-4} molar	38.3
	35.9
5.20×10^{-5} molar	43.5
	41.9
2.08×10^{-5} molar	42.3
	48.9

We explained previously that our spectroscopic equipment employed for measuring triplet extinction coefficients does not work too well when too-low concentrations of a studied compound are used [1]. We use the average of $\epsilon_T(670) = 45.6 \times 10^3$ l/mole cm obtained from the lowest concentration of $N_S = 2.08 \times 10^{-5}$ molar solution and present it in Table I. Although this value may carry larger experimental errors than the values obtained with higher concentrations, it will have the lowest errors resulting from dimer formation. We were not able to obtain meaningful data when even lower concentrations were employed. Photochemically, the dye was rather stable when excited with the line $\lambda_{cw} = 568.2$ nm.

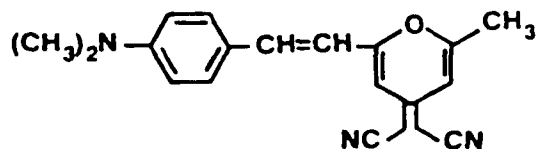


2. DCM

Some of the laser action and spectroscopic properties of DCM (4-dicyanomethylene-2-methyl-6-(p-dimethylaminestyrilyl)-4H-pyran has been described by Hammond [13]. Under excitation with the $\lambda_{cw} = 476.5$ -nm line, this dye was photochemically rather stable. A 2×10^{-4} molar solution yielded an $\epsilon_T(760) = 6.3 \times 10^3$ l/mole cm. The 1×10^3 molar solution gave 7.4 and 6.9×10^3 l/mole cm, respectively. In Table I, we used the average of the last two values.

Table I. Measured triplet extinction coefficients ϵ_T of laser dyes as a function of wavelength λ_{las} . λ_i (nm) is the wavelength at which I/OD_T was measured. I_{ex} is the maximum cw laser power (in mW) employed for excitation. λ_{cw} (nm) is the wavelength of the exciting cw laser line.

LASER DYE	λ_{las} (nm)					λ_i	I_{ex}	λ_{cw}
	$\epsilon_T (l \times 10^{-3} \ell / \text{mole cm})$					(nm)	(mW)	(nm)
DODC	630	650	690	710	730	670	50	568.2
	42.2	73.4	62.1	58.4	45.6	99.0		
DCM	610	630	650	670	690	760	40	476.5
	5.4	5.9	5.5	5.5	6.3	7.2		
KYTON RED	590	610	630	650	670	650	60	568.2
	7.6	7.4	6.7	5.2	2.4	5.2		
RHODAMINE 575	560	580	600	620	640	660	10	514.5
	3.3	6.6	6.0	5.6	5.6	5.1		
COUMARIN 523	500	520	540	560	580	580	20	454.5
	0.9	1.4	2.1	2.5	3.0	3.0		
COUMARIN 521	500	520	540	560	580	600	50	454.5
	6.5	5.1	4.0	3.3	3.2	3.1		
COUMARIN 504	480	500	520	540	560	620	25	454.5
	4.2	3.3	3.6	4.4	4.8	5.5		
COUMARIN 498	480	500	520	540	560	600	10	454.5
	0.8	1.4	2.0	2.7	2.6	3.2		
COUMARIN 490	470	490	510	550	570	530	20	351.1/ 363.8
	1.2	1.5	2.2	2.7	2.9	3.2		
LD 466	440	460	480	500	520	560	20	351.1/ 363.8
	1.0	1.5	1.9	2.9	4.4	7.0		
bis-MSB	410	420	440	460	480	520	60	351.1/ 363.8
	0.8	0.8	0.85	0.8	1.8	4.0		
OLIGO415	410	430	450	470	490	670	5	351.1/ 363.8
	2.9	2.4	2.2	2.8	3.8	75.3		
BBO	390	410	430	450	470	590	50	351.1/ 363.8
	13.2	19.6	22.2	13.7	13.5	48.5		

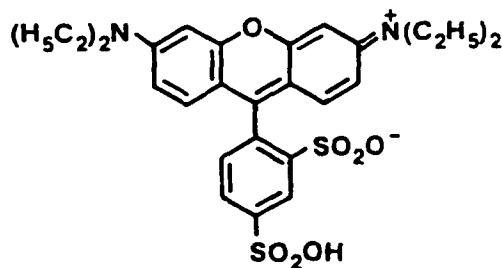


DCM

3. Sulforhodamine B

This dye is also known by the name Kyton Red. Laser action of this compound was reported by Gregg et al. [14].

Photochemically, this compound was not too stable. We therefore performed several measurements. A 2.1×10^{-4} molar solution yielded $\epsilon_T(650) = 4.3, 6.2, \text{ and } 5.4 \times 10^3 \text{ l/mole cm}$. A 1.05×10^{-4} molar solution: $5.5, 4.7, 5.8, \text{ and } 4.7 \times 10^3 \text{ l/mole cm}$. The value noted in Table I is the average of all seven measurements.



Kiton Red 620

4. Rhodamine 575

4.1 Triplet Extinction Coefficients by McClure's Method.

Drexhage reported laser action from this compound under flashlamp excitation [15]. Exciting with a $\lambda_{cw} = 514.5\text{-nm}$ line, this dye showed good photostability. We also observed a rather large triplet optical density OD_T attributable to the presence of a long triplet-state lifetime. A 2×10^{-4} molar solution gave $\epsilon_T(660) = 5.0 \times 10^3 \text{ l/mole cm}$. A 1×10^{-4} molar solution yielded $6.0 \text{ and } 6.2 \times 10^3 \text{ l/mole cm}$. The average of the last two values is shown in Table I.

4.2 Triplet Extinction Coefficients by the Improved Depletion Method.

The S-S absorption maximum of this dye is located at about 518 nm. Exciting a 1×10^{-4} molar solution with the $\lambda_{cw} = 501.7\text{-nm}$ line, a rather large depletion was observed at the onset of S-S absorption. To reduce unabsorbed excitation laser radiation, an OG530 Schott optical-glass filter was used in the F_1 position [7]. A plot of the measured OD_{S-T} values as

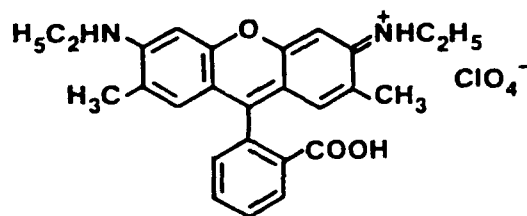
functions of wavelength is shown in Figure 1. It should be noted that $OD_{S+T} = OD_T$ for $\epsilon_S = 0$. The isospectric point λ_c at 551 nm was easily determined. At this point, we measured $\epsilon_S = 7.6 \times 10^3$ l/mole cm $= \epsilon_T$. Extrapolating OD_T by a straight line to 551 nm yields $OD_T = 0.15 = N_T \epsilon_T d$, or $N_T = 6.9 \times 10^{-5}$ molar. With $OD_T(600) = 0.128 = N_T \epsilon_T(600)d$, we obtain $\epsilon_T(600) = 6.5 \times 10^3$ l/mole cm. This value is in good agreement with $\epsilon_T(600) = 6.0 \times 10^3$ l/mole cm shown in Table I. Since the method we just employed does not use any kinetic considerations, it provides strong support for the validity of McClure's method for providing meaningful ϵ_T values. The $\epsilon_S(\lambda_c)$ value was measured at the temperature of liquid nitrogen and corrected for contraction. Some of the shortest-wavelength ϵ_T values listed in Table I could be improved by taking into account underlying weak S-S absorption. This can be accomplished by rewriting equation (11):

$$\epsilon_T = \frac{OD_{S+T}}{N_T d} + \epsilon_S \quad (13)$$

Using ϵ_S values measured at room temperature should introduce only small errors in the obtained ϵ_T values.

4.3. Measuring OD_T Values as a Function of I_{ex} .

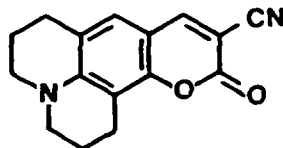
Instead of plotting $1/OD_T$ versus $1/I_{ex}$ to obtain $1/OD_T^\infty$, we plotted OD_T as a function of I_{ex} and present the obtained curve in figure 2. It is apparent from this figure that, at small excitation intensities I_{ex} , the linear relationship $OD_T = AI_{ex}$ holds.



Rhodamine 575

5. Coumarin 523

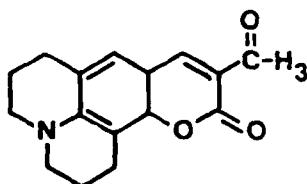
This dye was synthesized and tested by Reynolds and Drexhage [16]. Exciting the dye solutions with $\lambda_{cw} = 454.5$ -nm line, this dye was rather stable photochemically. A 2×10^{-4} molar solution yielded $\epsilon_T(580) = 2.1 \times 10^3$ l/mole cm. Using a 1×10^{-4} molar solution, ϵ_T values of 2.9 and 3.0×10^3 l/mole cm were recorded. Again, the average of the last two values is shown in Table I.



Coumarin 523

6. Coumarin 521

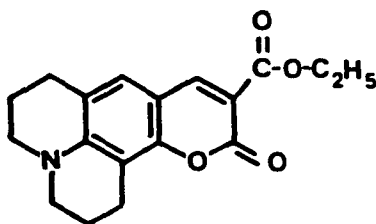
This dye was also reported in [16]. It was rather stable photochemically, with $\lambda_{cw} = 454.5$ -nm excitation. However, rather low OD_T values were obtained, most likely the result of a small triplet-state lifetime present in this compound. Using a 2×10^{-4} molar solution, we obtained $\epsilon_T(600) = 3.1 \times 10^3$ l/mole cm. With a 1×10^{-4} molar solution, $\epsilon_T(600) = 2.9$ and 3.2×10^3 l/mole cm were measured. The value shown in Table I is the average of all three measurements.



Coumarin 521

7. Coumarin 504

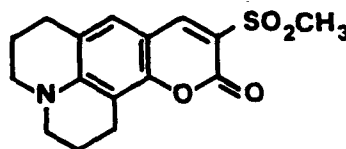
Among the known Coumarin laser dyes, Coumarin 504 has one of the highest efficiencies. It is another dye reported in [16]. It was rather stable under $\lambda_{cw} = 454.5$ -nm excitation. Employing a 2×10^{-4} molar solution, we measured $\epsilon_T(620) = 3.2$ and 3.3×10^3 l/mole cm. The 1×10^{-4} molar solution gave 5.5 and 5.5×10^3 l/mole cm. The average of the last two values is shown in Table I.



Coumarin 504

8. Coumarin 498

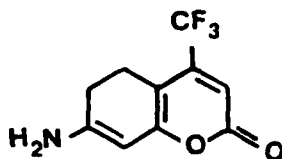
Laser action under flashlamp excitation from this laser dye was reported by Fletcher et al. [17]. This dye was also rather stable under $\lambda_{cw} = 454.5$ -nm excitation. A 2.33×10^{-4} molar solution yielded $\epsilon_T(600) = 3.0 \times 10^3$ l/mole cm. The 1.16×10^{-4} molar solution yielded 3.2 and 3.2×10^3 l/mole cm. The average of the last two values is reported in Table I.



Coumarin 498

9. Coumarin 490

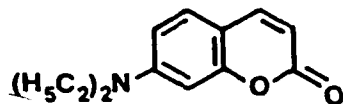
This fluorinated laser dye was synthesized and tested by Schimitschek et al. [18]. Under excitation with the $\lambda_{cw} = 351.1/363.8$ -nm line, it showed some photodecomposition. A 2.7×10^{-4} molar solution gave $\epsilon_T(530) = 3.1$ and 3.5×10^3 l/mole cm. The 1.35×10^{-4} molar solution gave 3.0×10^3 l/mole cm. The average of all three values is listed in Table I.



Coumarin 490

10. LD466

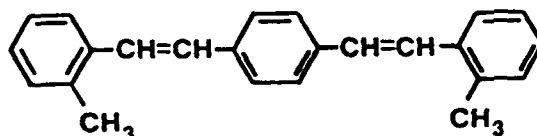
This dye was synthesized by Schimitschek et al. [18]. Excited with the $\lambda_{cw} = 351.1/363.8$ -nm lines, it showed some photodecomposition. A 2.2×10^{-4} molar solution gave $\epsilon_T(560) = 6.9 \times 10^3$ l/mole cm and the 1.1×10^{-4} molar solution gave 6.8 and 7.2×10^3 l/mole cm. The average of all three values is reported in Table I.



Coumarin 466

11. bis-MSB

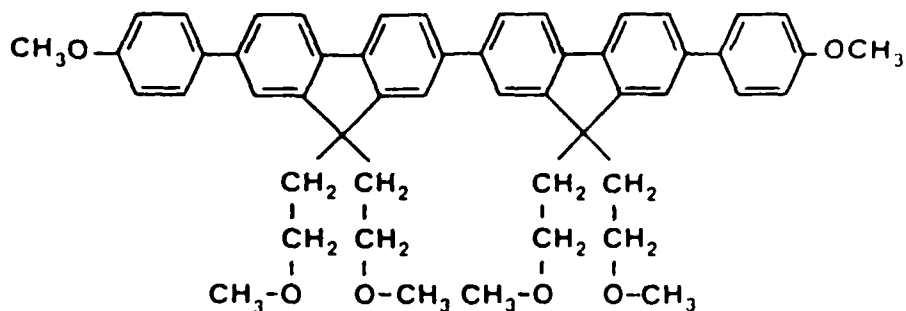
Using a 50-ns-risetime flashlamp, laser action from bis-MSB(1,4-bis(2-methylstyryl)-benzene) was reported by Furumoto and Cecon [19]. This dye was rather stable photochemically under excitation with $\lambda_{cw} = 351.1/363.8$ -nm. A 5×10^{-4} molar solution yielded $\epsilon_T(520) = 1.8 \times 10^3$ l/mole cm. The 2.0×10^{-4} molar solution gave a $\epsilon_T(520) = 3.8$ and 4.2×10^3 l/mole cm. The average of these two values is shown in Table I.



bis-MBS

12. OLIGO415

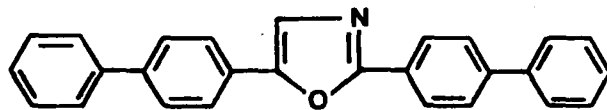
This new laser dye was designed and synthesized by Kauffman. Like 2,7-bis(4-methoxyphenyl)-9,9-dipropylfluorene discussed in paper I, OLIGO415 is another example of an improved laser dye [22] possessing a favorable A_2c constellation [23]. OLIGO415 exhibited a rather long triplet-state lifetime and was rather stable photochemically under $\lambda_{cw} = 351.1, 363.8$ -nm excitation. Nevertheless, a $1/I_{ex}$ versus $1/OD_T$ plot yielded steep lines. Small experimental errors resulted in OD_T^∞ values that showed some deviations. We performed several measurements to reduce errors. With a 1×10^{-4} molar solution, we obtained $\epsilon_T(670) = 71.7$ l/mole cm. A 5×10^{-5} molar solution yielded $\epsilon_T(670) = 92.0, 86.9, 71.5,$ and 54.7×10^3 l/mole cm, respectively. The average of all these five measurements is presented in Table I.



Oligo 415

13. BBO

Employing a short-risetime flashlamp, laser action from BBO(2,5-bis(4-biphenyl)-oxazole) was observed by Rubinov and Mostovnikov [20]. Under excitation with $\lambda_{cw} = 351.1/363.8$ nm, this compound showed some photodecomposition. A 2×10^{-4} molar solution gave $\epsilon_T(590) = 31 \times 10^3$ l/mole cm. A 1×10^{-4} molar solution: $\epsilon_T(590) = 48.3$ and 48.7×10^3 l/mole cm. The average of the last two values is reported in Table I. According to Berlman [20], the quantum fluorescence yield of this compound is rather high ($\phi_F = 0.92$). The less than spectacular laser-action properties of this compound are the result of the rather large $\epsilon_T(\lambda_{las})$ values shown in Table I.



B B O

B. Discussion

Inspecting the ϵ_T values of the laser dyes presented in Table I, the dyes show ϵ_T at about 1×10^3 l/mole cm or larger. This was also the case for the ϵ_T values presented in table I of paper I. These ϵ_T values cannot be termed small. To explain the reasons why presently known laser dyes have these rather large ϵ_T values, we offer the following explanation.

The presense of benzene (and its heterocyclics) in most organic compounds is responsible for introducing the spectroscopic property of fluorescence. Virtually all aliphatic compounds exhibit no fluorescence. The very few exeptions known to fluoresce have generally low quantum fluorescence yields. Although there are many thousands of aromatic compounds known to show strong fluorescence ($\phi_F \approx 1$), a suprisingly small number show laser action under flashlamp excitation. Although Rhodamine 6G has been known since 1967, no new laser dye has dethroned it as being one of the most efficient laser dyes.

Reviewing experimental data on T-T absorption measurement of organic compounds in the literature [3], it is apparent that all aromatic compounds listed in this review paper possess strong (to very strong) T-T absorption stretching from their fluorescence spectral region to longer wavelengths. Considering aromatic compounds that have only one T-T absorption band in this spectral region, the following is concluded: only if this strong to very strong T-T absorption band is located far away (to the red) of the fluorescence spectral region, will small T-T absorption be present. This spectral arrangement of electronic transitions has been called an A₂a (or A₂c) constellation [19,20]. If, in addition, the compound also possesses a high quantum fluorescence yield ϕ_F , laser action is generally observed. Examples of laser dyes with A₂a or A₂c constellations are the Coumarins [7,19,20]. The xanthene laser dyes also belong to this group. Zanker and Miethke observed a strong T-T absorption band at about 1,200 nm in Fluorescein [21]. In addition, (laser dyes derived from trans-stilbene [22], like bis-MBS; Stilbene I [1] and II; and the oligophenylene laser dyes [20].) A typical example presenting these laser dyes is OLIGO415, shown in Figure 4. If the strong T-T absorption band were at shorter wavelengths, laser action efficiency would diminish. Aromatic compounds for which this strong T-T absorption band is positioned further into the red portion of the spectrum may not exist.

If, for example, laser dyes could be found or synthesized that have electronic transitions located at the same spectral locations as OLIGO415, but possess a T-T absorption band that is 10 times weaker, we would have $\epsilon_T(\lambda_F) = 2 \times 10^2 \text{ l/mole cm}$. This, together with a high quantum fluorescence yield, should assure very efficient laser action. The search for new laser dyes should possibly concentrate on organic compounds (*quasi*-aromatic heterocyclics) that exhibit strong fluorescence but do not contain any homocyclic and/or heterocyclic aromatic groups. Some of these compounds seem to have low T-T absorption near or over their fluorescence spectral regions.

Laser dyes were recently discovered in the *quasi*-aromatics *syn*-9,10-dioxabimanes[*syn*-(R₂,R₁) bimanes] [23] and pyrromethene-BF₂ complexes [24,25].

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REFERENCES

1. T.G. Pavlopoulos and D.J. Golich, *J. Appl. Phys.* **64**, 521 (1988).
2. D.J. McClure, *J. Chem. Phys.* **19**, 670 (1951).
3. I. Carmichael and G.L. Hug, *Phys. and Chem. Ref. Data* **15**, 1, (1986).
4. T.G. Pavlopoulos, *J. Opt. Soc. Am.* **63**, 180 (1973).
5. G. Porter and M.W. Windsor, *Proc. Roy. Soc. A*, **245**, 238 (1958).
6. H. Labhart and W. Heinzelmann, *Organic Molecular Photophysics*, Vol. I, Ed. J. B. Birks, Wiley and Sons, 1973.
7. T.G. Pavlopoulos, *Spectrochim. Acta* **43A**, 1201 (1987).
8. E.G. Arthurs, D.J. Bradley, and A.G. Roddie, *Appl. Phys. Lett.* **20**, 125 (1972).
9. M. Young, *Appl. Optics* **18**, 3212 (1979).
10. A. Watanabe et al., *IEEE J. Quantum Electron.* **QE-19**, 533 (1983).
11. M. Maeda and Y. Miyazoe, *Jpn. J. Appl. Phys.* **11**, 692 (1972).
12. D.N. Dempster, T. Morrow, R. Rankin, and G.F. Thompson, *J. Chem. Soc.*, **68**, 1479 (1972). *Faraday Trans.* **68**, 1479 (1972).
13. P.R. Hammond, *Optics Comm.* **29**, 331 (1979).
14. D.W. Gregg, M.R. Querry, J.B. Marling, S.J. Thomas, C.V. Dobler, N.J. Davies, and J.F. Belew, *IEEE J. Quantum Electron.* **QE-6**, 270 (1970).
15. K.H. Drexhage, *Laser Focus* **9**, 35 (1973).
16. G.A. Reynolds and K.H. Drexhage, *Optics Comm.* **13**, 222 (1975).
17. A.N. Fletcher, D.E. Bliss, and J.M. Kauffman, *Optics Comm.* **47**, 57 (1983).
18. E.J. Schimitschek, J.A. Trias, P.R. Hammond, and R.L. Atkins, *Optics Comm.* **11**, 352 (1974).
19. T.G. Pavlopoulos, *IEEE J.* **QE-9**, 510 (1973).
20. T.G. Pavlopoulos and P.R. Hammond, *J. Am. Chem. Soc.* **96**, 6568 (1974).
21. V. Zanker and E. Miethke, *Z. Naturforschg.* **12a**, 385 (1957).
22. T.G. Pavlopoulos and D.G. Taylor III, *Spectrochim. Acta* **41A**, 1357 (1985).
23. T.G. Pavlopoulos, J.H. Boyer, I.R. Politzer, and C.M. Lau, *Optics Comm.* **64**, 367, (1987).
24. T.G. Pavlopoulos, M. Shah, and J.H. Boyer, *Appl. Optics* **27**, 4998 (1988).
25. T.G. Pavlopoulos, M. Shah, and J.H. Boyer, *Optics Comm.*, in print.

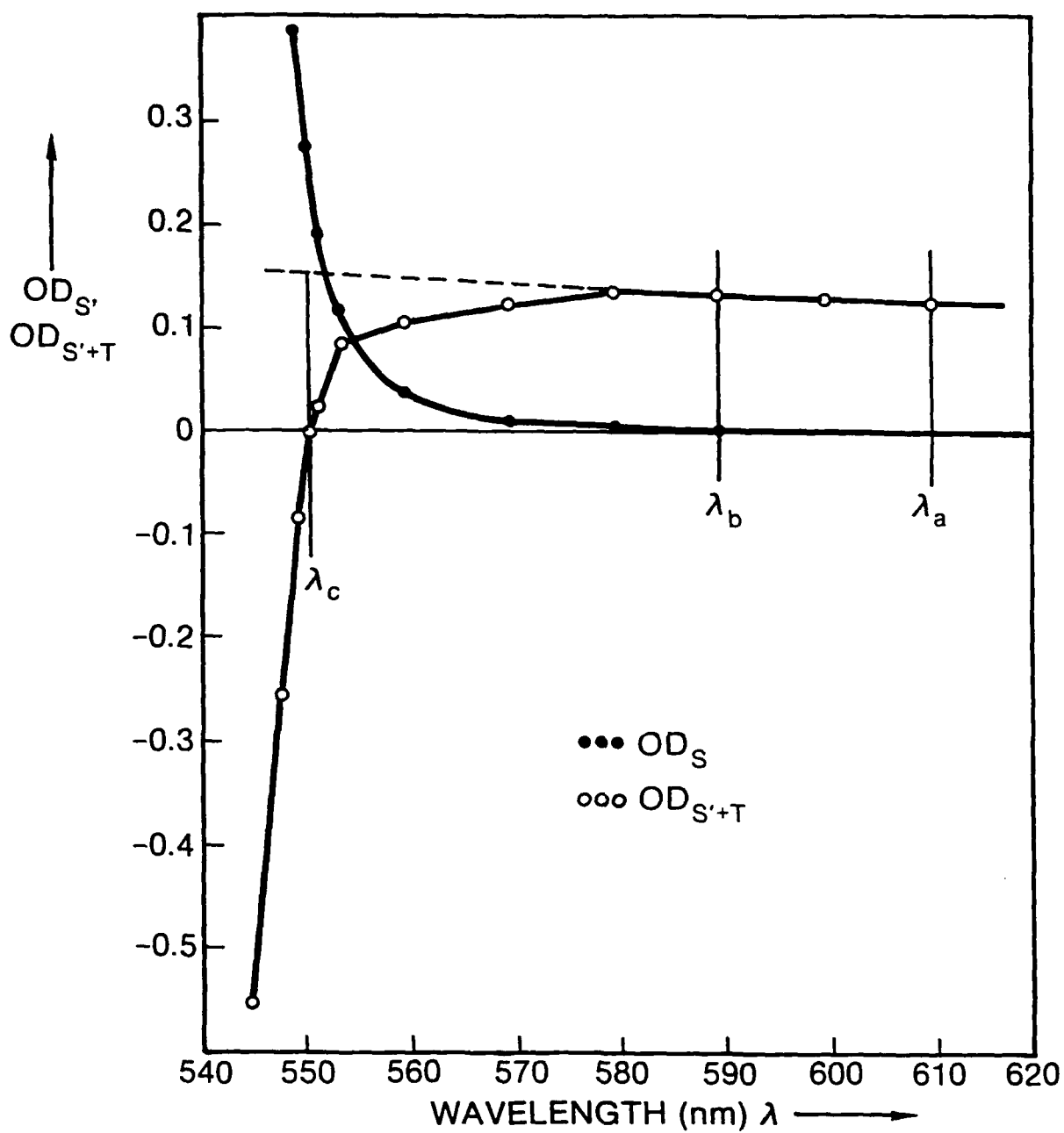


Figure 1. Plot of (singlet) optical density OD_S and triplet optical density $OD_{S'+T}$ ($= OD_T$ for $\epsilon_S = 0$) versus wavelength of Rhodamine 575. At λ_c we have $OD_{S'+T} = 0$ and $\epsilon_S(\lambda_c) = \epsilon_T(\lambda_c)$.

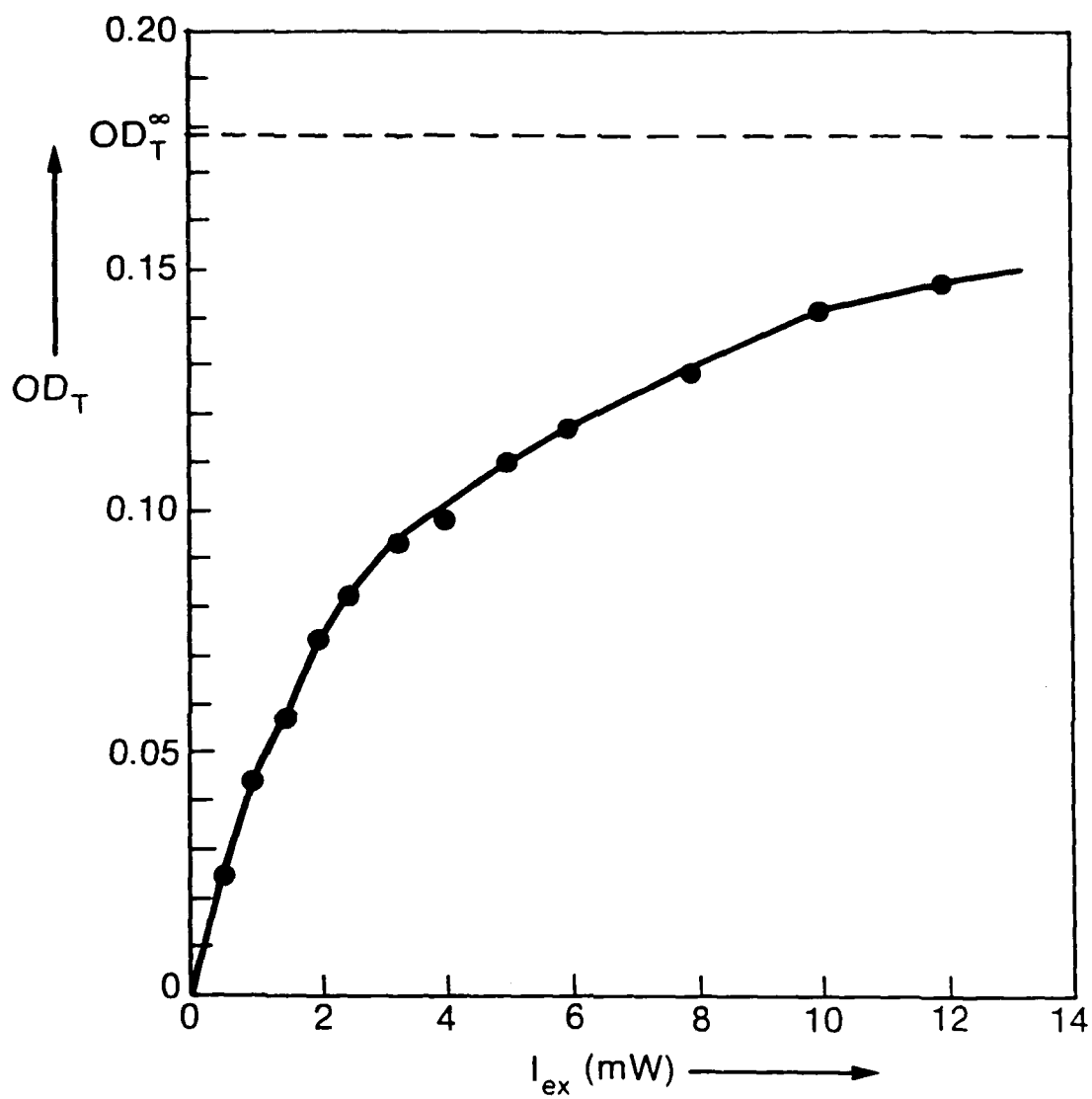


Figure 2. Plot of triplet optical density OD_T as function of cw laser excitation intensity (power) I_{ex} . OD_T^{∞} was obtained by plotting $1/OD_T$ versus $1/I_{ex}$ and extrapolating $1/I_{ex} \rightarrow 0$.

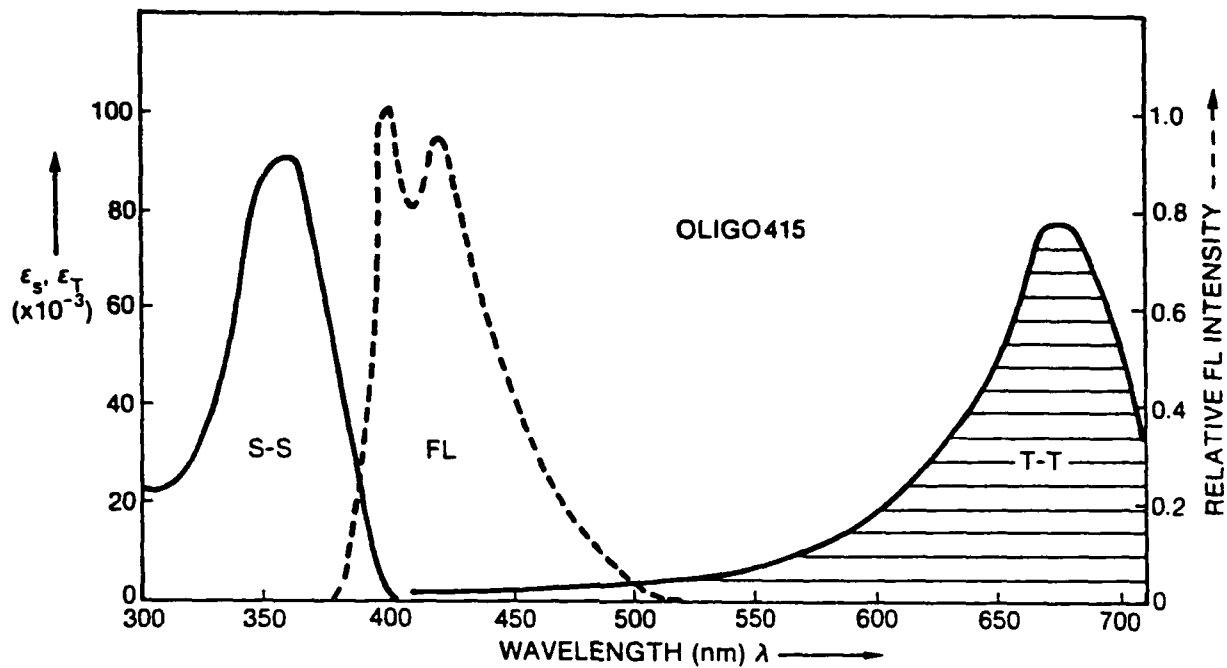


Figure 3. Fluorescence FL, S-S absorption, and T-T absorption spectra as a function of wavelength λ of OLIGO415. To measure the fluorescence and S-S absorption spectra, a 1×10^{-4} molar solution of 2-methyltetrahydrofuran was used.

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